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6. AUTHORS
Luke M. Haverhals

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Bradley University
1501 W. Bradley Ave.

Peoria, IL 61625 -0003

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14. ABSTRACT
This report details the procurement and integration of an infrared (IR) spectrometer (Thermo Scientific - Nicolet iS50R Spectrometer) into our electrochemistry program. The instrument is being utilized to characterize ionic liquid-based (IL-based) electrolyte systems via simultaneous electrochemical and spectroscopic studies. These studies are enabling us to understanding the microscopic (molecular and ionic) dynamics at electrolyte/electrode interfaces. This information is important for the development of enhanced energy conversion processes and

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Report Title

Final Report: ARO Research Instrumentation Program - IR Spectrometer Procurement

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

C. Zibart, D. Parr, B. Egan, H. Morris, A. Tivanski, L. M. Haverhals, “Investigation of Structure at Gold-Ionic Liquid Electrolyte Interfaces”, Argonne National Laboratory 24th Annual Undergraduate Symposium, 7 November, 2014, Argonne, Illinois.

C. Meunier, E. Roberts, E. Remsen, L. M. Haverhals, “Investigation of Mass Transport in Mesoporous Semiconducting Thin Film Electrodes”, Argonne National Laboratory 24th Annual Undergraduate Symposium, 7 November, 2014, Argonne, Illinois.

N. Dexter, E. Larson, D. Gray, C. Meunier, L. Moore, K. Pelphrey, B. Tisserat, L. M. Haverhals, “Sustainable and Renewable Biocomposites”, Argonne National Laboratory 24th Annual Undergraduate Symposium, 7 November, 2014, Argonne, Illinois.

E. Larson, N. Dexter, D. Gray, B. Kowalowski, R Cormier, G. Cote, L. M Haverhals, “Functional Biosynthetic Films”, Argonne National Laboratory 24th Annual Undergraduate Symposium, 7 November, 2014, Argonne, Illinois.

C. Zibart, B. Egan, and D. Parr, H. Morris, Alexei Tivanski, L. M. Haverhals, “Microstructure at the Ionic Liquid/Electrode Interface”, 226th ECS Meeting, 8 October, 2014, Cancun, Mexico.

C. Meunier, D. Gray, E. Larson, N. Dexter, L. Moore, K. Pelphrey, B. Tisserat, L. M. Haverhals, “Rethinking ‘Green’: Sustainable, Renewable, and Functional Biocomposites”, ACS Heartland 75th Anniversary Gala, 4 October, 2014, Peoria, Illinois.

Number of Presentations: 6.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

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NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

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NAME	PERCENT_SUPPORTED

FTE Equivalent:
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This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

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Names of Personnel receiving masters degrees

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Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

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Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

FINAL REPORT

"ARO Research Instrumentation Program - IR Spectrometer Procurement"

Proposal #: 64964CHRI
Agreement #: W911NF1410028
01/15/2014 – 01/14/2015

Prepared by: Luke Haverhals
Assistant Professor
Department of Chemistry
Bradley University

Abstract

This report details the procurement and integration of an infrared (IR) spectrometer (Thermo Scientific - Nicolet iS50R Spectrometer) into our electrochemistry program. The instrument is being utilized to characterize ionic liquid-based (IL-based) electrolyte systems via simultaneous electrochemical and spectroscopic studies. These studies are enabling us to understanding the microscopic (molecular and ionic) dynamics at electrolyte/electrode interfaces. This information is important for the development of enhanced energy conversion processes and devices (e.g., supercapacitors). The Nicolet iS50R spectrometer has been synchronized with a potentiostat to perform surface enhanced infrared absorption (SEIRA) spectroscopy during electrochemical (voltammetric) perturbation. The spectrometer has also been utilized to help us characterize biomaterials before and after processing in a separate project that aims to create robust, functional biocomposites. In particular, we are interested to develop tough bio-based composites for energy storage and water remediation applications. Sample data from these ongoing efforts are demonstrated in this report.

Statement of the Problem Studied

Our group is interested in understanding the interface between the electrode and electrolytes. Knowledge in this area is important because chemical interactions at the electrode/electrolyte interface determine the type, rate, and efficiency of electron transfer processes that control device performance.[1,2] We have chosen to pursue studies that involve simultaneous infrared (IR) spectroscopy with electrochemical perturbation. We have modeled our work after other researchers that have utilized these techniques with 'traditional' electrolytes (e.g., aqueous systems) at metal electrodes.[3] However, we have turned our focus to ionic liquid electrolytes which, to date, have been largely unexplored. In the past decade, ionic liquids (ILs) have been targeted as electrolytes for a wide variety of electrochemical applications however, there is presently a knowledge gap with respect to characterizations of the interfaces between electrodes and IL-based systems.[3] This report shows our progress towards building capabilities that will allow us to systematically study dynamic interactions at the interface between ILs and electrode surfaces.

Summary of Important Results

- We have performed simultaneous electrochemical and spectroscopic (SEIRA) experiments that probe the interactions of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIm TFSI) at nanostructured gold electrodes. Research assistants have been trained and are performing spectroelectrochemical experiments with mixed systems (e.g., EMIm TFSI + acetonitrile).
- Our group has begun to work to improve upon bio-based superconducting electrode materials in collaboration with Paul Trulove's group at the US Naval Academy.

<u>Simultaneous Electrochemical + SEIRA Experiments</u>

When a potential is applied to an electrode, physics still dictates that charge be compensated between the electrode and solution as:

$$-\sigma_{\text{metal electrode}} = \sigma_{\text{solultion}} \qquad \textbf{Equation 1}$$

In the case of pure ionic liquid (IL) solvents, the fact that the solution is composed solely of ions puts unique constraints on the way in which ions can reorganize to form a potential gradient, **Figure 1**. To date, there remains debate on the exact nature of the structure of ILs at charged surfaces. Additionally,

there is evidence that the time scales over which the solution can reorganize to changes in potential are lengthened significantly primarily due to ion-ion interactions, hydrogen bonding, et cetera that increase the viscosity. This raises the possibility of manipulating the structure of ILs by appropriate waveforms (time scales) that probe kinetic and thermodynamic parameters of the electrode/electrolyte interface.

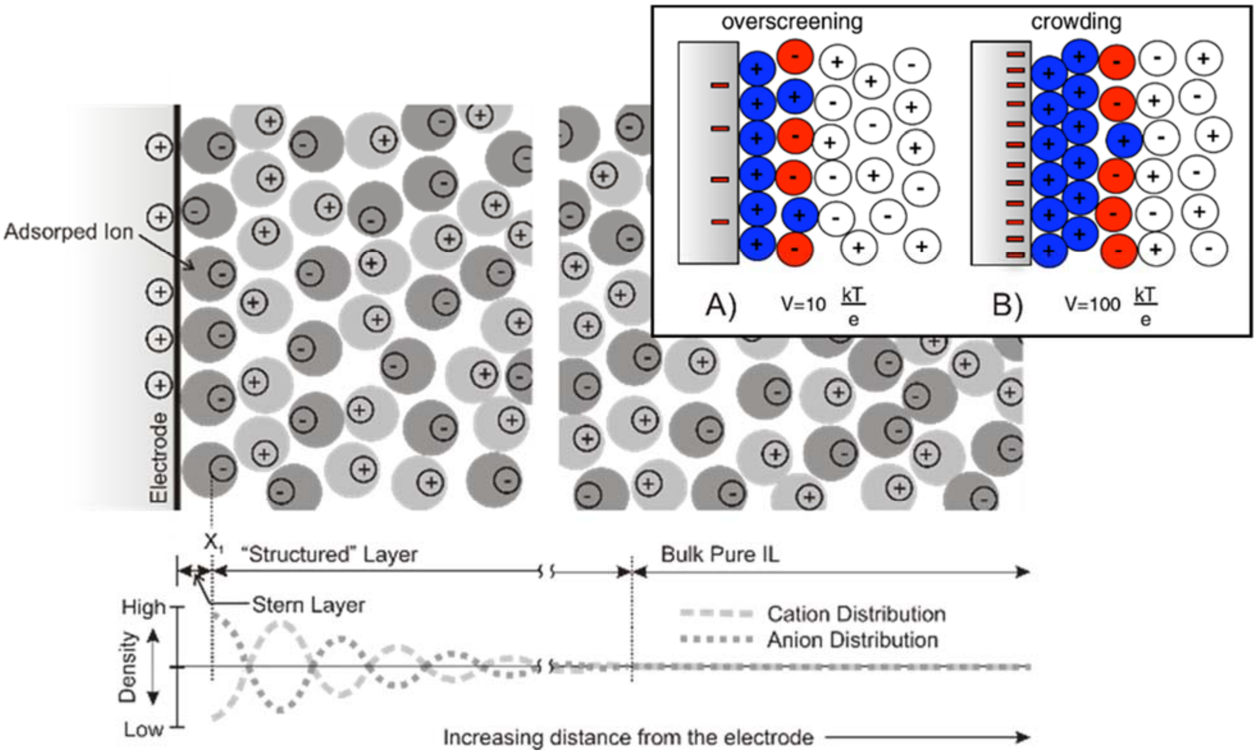

Figure 1: Cartoons illustrating the double layer in for an IL. (Not to scale, nor should shapes of ions be taken literally.) The inset in the upper right corner is from[4]: M. Z. Bazant, B. D. Storey, A. A. Kornyshev, *Phys. Rev. Lett.*, **2011**, *106*, 046102 1-4. Our group is working on experiments that probe the true structure and nature of ILs at metal surfaces.

Figure 2 shows a spectroelectrochemical cell in the standard Kretschmann geometry for performing SEIRA measurements.[5] Infrared (IR) light is directed through an attenuated total reflectance (ATR) crystal onto which a thin (several nm thick) nanostructured film metal electrode has been deposited. Light penetrates the electrode from the back and excites surface plasmons at the electrode/electrolyte interface. Penetration of the evanescent wave into solution is shallow (<100 nm) compared to traditional ATR (~1-5 μm with no metal film) and is strongly dependent on the types of materials (refractive indices), angle of incidence, the wavelength of light, and the thickness (of the film electrode). In the case of SEIRA, thin 'island-like' films (but still conductive) promote surface plasmon resonance that amplifies the absorbance of adsorbed species in addition to providing a larger interfacial surface area (than a smooth metal film). As IR light excites surface plasmons, the dipole moments (μ) of adsorbed species at the metal surface (at right) interact constructively or destructively depending on the geometry of interaction. Infrared absorptions are thus indicative of the type of adsorbed species as well as the average orientation. With a sufficiently fast and sensitive spectrometer/detector, SEIRA spectroscopy provides insight as to the real-time structural dynamics of ILs when performed with simultaneous manipulation of the electrode potential (e.g., during cyclic voltammetry).

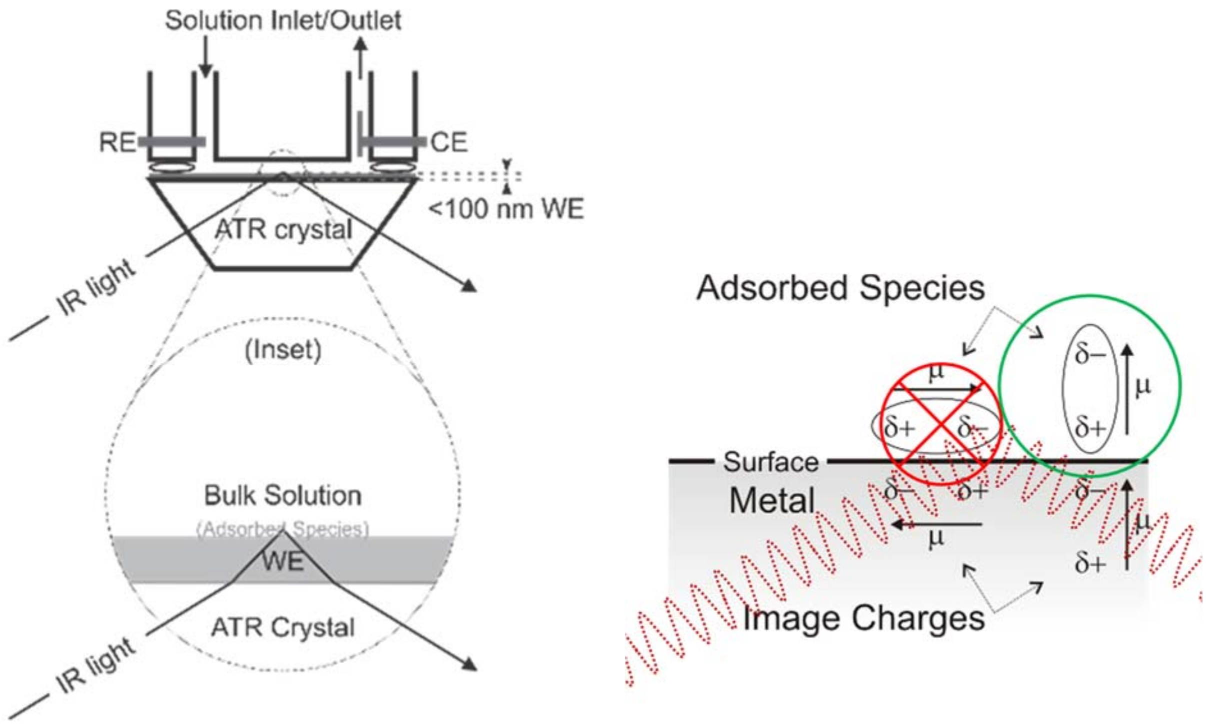

Figure 2: Cartoons illustrating the surface enhanced infrared absorption (SEIRA) spectroscopy via an attenuated total reflectance (ATR) crystal modified with a nanostructured metal film working electrode. The so called, 'Kretschmann' ATR geometry (at left) has a thin (<~100 nm) metal film which enables simultaneous spectroscopic and electrochemical experiments.[5]

Initial data collected utilizing the new IR spectrometer are shown in **Figure 3**. Here, we have employed the Kretschmann cell geometry with a standard three electrode system controlled and measured by a potentiostat. Data are the SEIRA absorbance difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during potential step experiments. Spectra are stacked on a relative scale for viewing purposes. Spectra for potentials held at 0.0, -0.5, -0.7, -1.0, -1.5, -2.0, and -2.5 V, respectively, have been background subtracted by a second experiment at 0.0 V. These data thus emphasize how absorbance changes (from 0.0 V) as the potential is stepped to more negative potential. As should be expected, vibrational modes for the anion become less pronounced and indicate the density of anions decreases near the electrode as the potential becomes more negative. Note these data indicate a 'thermodynamic' structure in that, since the potential was held for a relatively long (minutes) time scale, the IL solution has time to rearranged in ways that minimize potential energy.

Data shown in **Figures 4** and **5** demonstrate spectroelectrochemical that probe system dynamics. (Spectral data are offset for clarity.) These data are the difference spectra for cyclic voltammetric experiments. Data detail an evolving, dynamic system as EMIm TFSI moves in response to the voltammetric perturbation. In this experiment, 10 CV experiments were performed in succession. The scan rate was fixed at 70 mV/s. In **Figure 4**, spectral data for the first CV of the series was recorded at +1.2 V and was utilized as the background (subtractive) scan. (This is denoted by the red box in the waveform shown at the upper left of the figure.) Spectral differences for the 5th, 6th, 7th, 8th, 9th, and 10th CVs (at +1.2 V) in the series are produced by subtracting the spectral data collected during the 1st CV. (The relative timing is denoted by the color coordinated boxes in the upper left-hand waveform inset.) The shaded regions denote the approximate position of absorption bands for symmetric (ν_s) and

asymmetric (ν_{as}) vibrational modes for the TFSI anion: 1055 cm^{-1} – ν_{as}(SNS), 1134 cm^{-1} – ν_s(SO_2), 1221 cm^{-1} – ν_{as}(CF_3), 1238 cm^{-1} – ν_s(CF_3), 1327 cm^{-1} – ν_{as}(SO_2), and 1357 cm^{-1} – ν_{as}(SO_2).[10] The data show an increase in the concentration of anion at the surface as the system evolves.

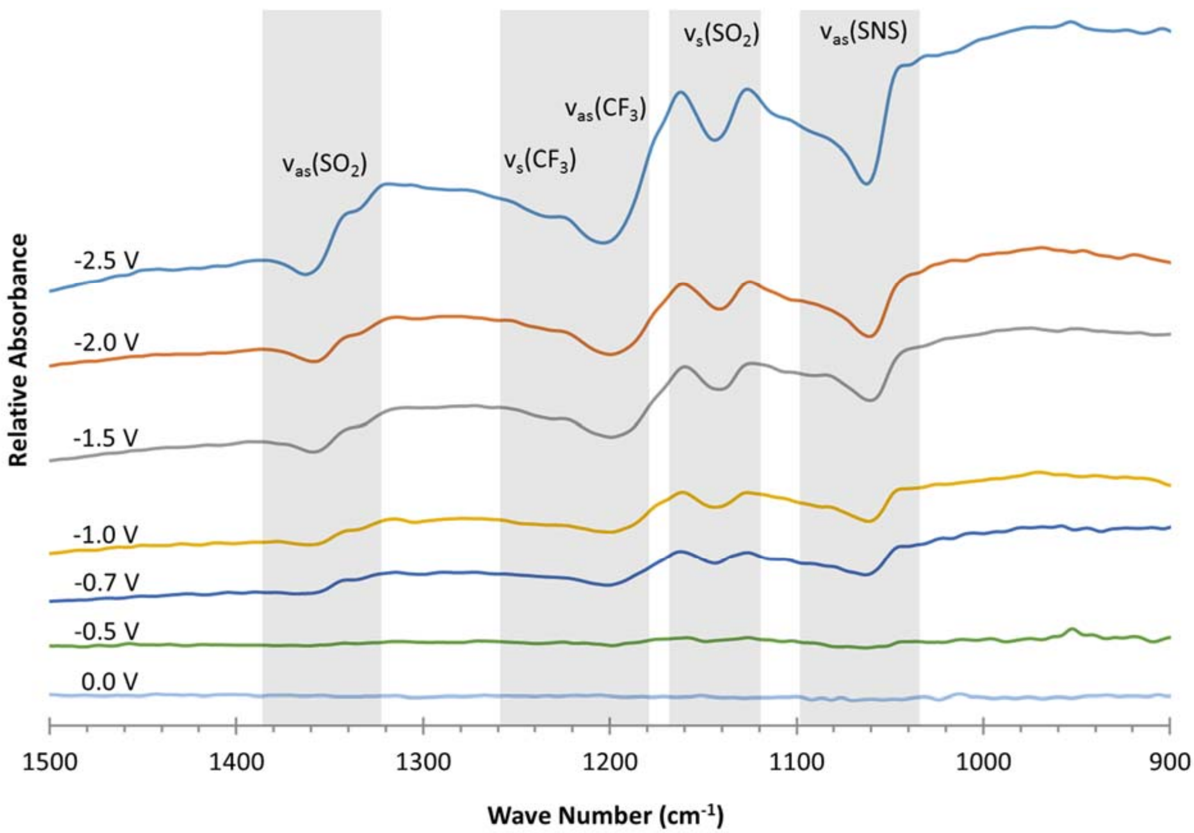

Figure 3: Data are the SEIRA absorbance difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during potential step experiments. Spectra are stacked on a relative scale for viewing purposes.

Data demonstrated in **Figure 4** are reasonable since the electrode is poised positive while data was collected (at these particular points) and therefore attracts anions. However, it is interesting to note (counterintuitive) that **Figure 5**, which is recorded while the working electrode is poised at -2.0 V also shows a system that evolves to move more anions near the electrode surface. Relative to the first CV, cycles 2 and 3 show less overall anion concentration in the difference spectra. The 4th cycle is relatively flat and implies the amount of anion is roughly similar to the first cycle. From the 5th cycle onward, the difference spectra indicate more anion is building up at an electrode surface (relative to the starting concentration) while poised to a strongly negative potential. This somewhat pyridoxal result is mostly likely explained by the combination of the scan rate (time scale of the experiment) with the viscosity of the IL system interrogated. In other words, structural hysteresis that involves a system of associated cations and anions that cannot move in time with the imposed waveform. We believe this to be an interesting result, however, because it suggests that the right combination of waveform (shape and timescale) with electrolyte system may allow the creation of 'kinetic' structures not otherwise observed under 'thermodynamic' (e.g., slow experimental) conditions.

As we move forward, we are trying to quantitatively assess the dynamics of IL-based systems. In particular, we hope to relate the observed dynamic behavior to the viscosity of the electrolyte solution. To this end and to simplify data analyses, we will move from CV to potential step experiments in attempt to capture double layer rearrangement as a function of time.

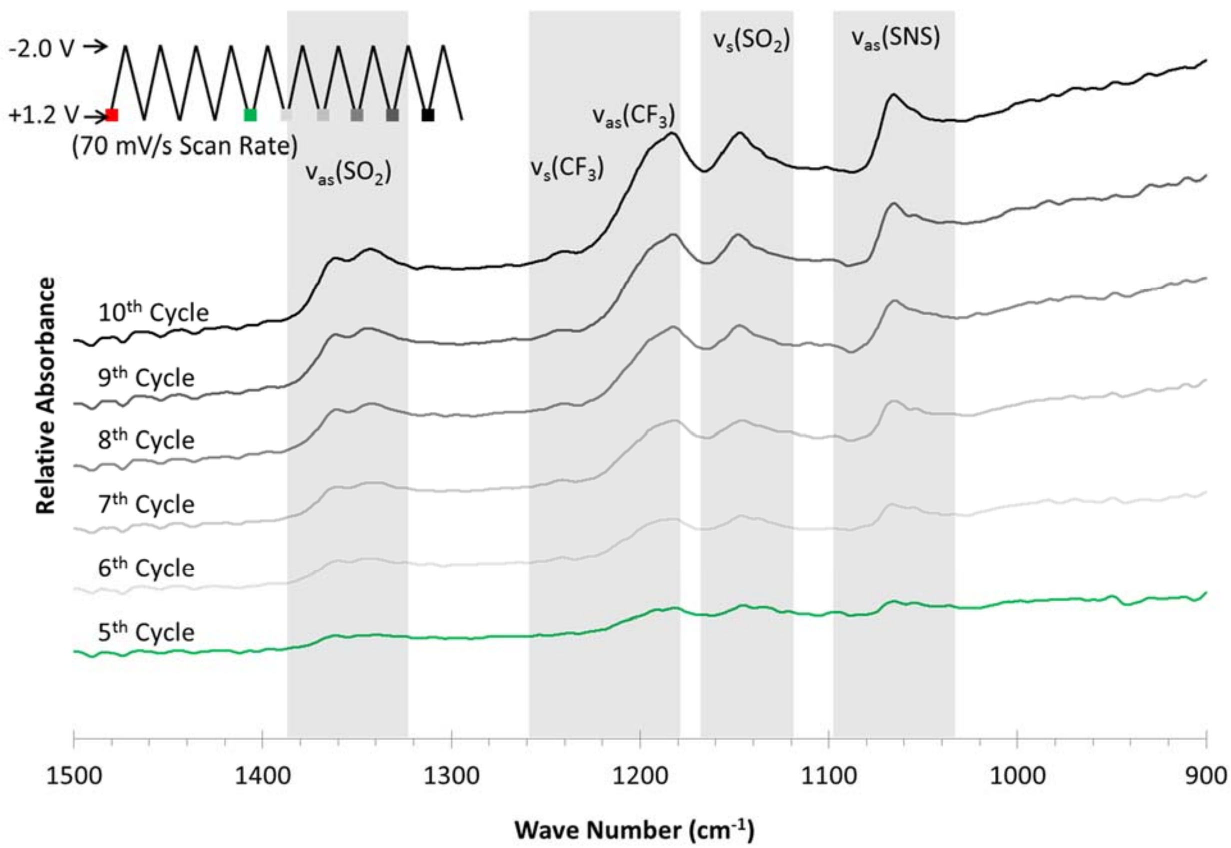

Figure 4: Data are the SEIRA absorbance difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during cyclic voltammetry (CV, scan rate = 70 mV/sec). Spectra are stacked on a relative scale for viewing purposes. Spectra for potential = +1.2 V during the 5^{th} to 10^{th} cycle, respectively, have been background subtracted utilizing the spectra taken during the first cycle (■). Data indicate hysteresis in that the anion concentration at the electrode appears to increase as cycles are repeated. This is consistent with literature data but also suggests that ‘kinetic’ structure might be controllably ‘built’ into the double layer by an appropriate waveform (time scale).

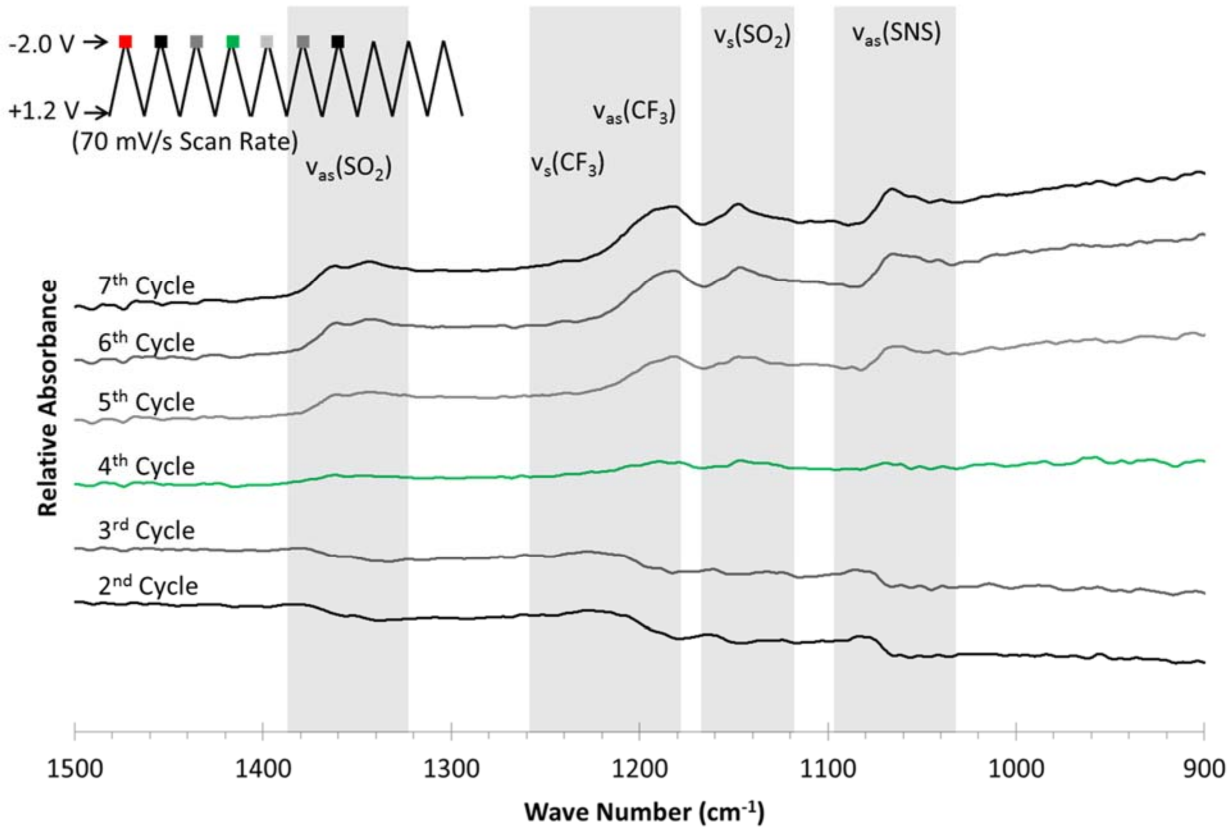

Figure 5: Data are the SEIRA absorbance difference spectra for EMIm TFSI at a 4.9 nm thick gold film electrode on a Ge ATR crystal during cyclic voltammetry (scan rate = 70 mV/sec). Spectra are stacked on a relative scale for viewing purposes. Spectra for potential = -2.0 V during the 2^{nd} to 7^{th} cycle, respectively, have been background subtracted utilizing the spectra taken during the first cycle (■). Data again indicate hysteresis in that the anion concentration at the electrode appears to increase as cycles are repeated. It is interesting to note that while cycles 2 and 3 show less anion near the electrode, cycles 4 to 7 display more anion character. Going forward, we are working to more directly comparing results for CV experiments with potential step-type experiments to determine what absolute structural differences ('kinetic' versus 'thermodynamic') may in fact exist.

Characterizations of Bio-based Composites

Simultaneous to SEIRA experimentation, we are working on new bio-based electrode materials. **Figure 6** is data for the modification of cotton yarns. In previous collaborative work with researchers at the US Naval Academy and Drexel University, cotton yarns have been demonstrated as suitable substrates for textile-based energy storage.[6] Data in **Figure 6** represents initial efforts to improve upon this seminal work. These data show yarn before and after IL-based solvents have been utilized to process cotton yarn. The new IR spectrometer has been useful to characterize new processing techniques.

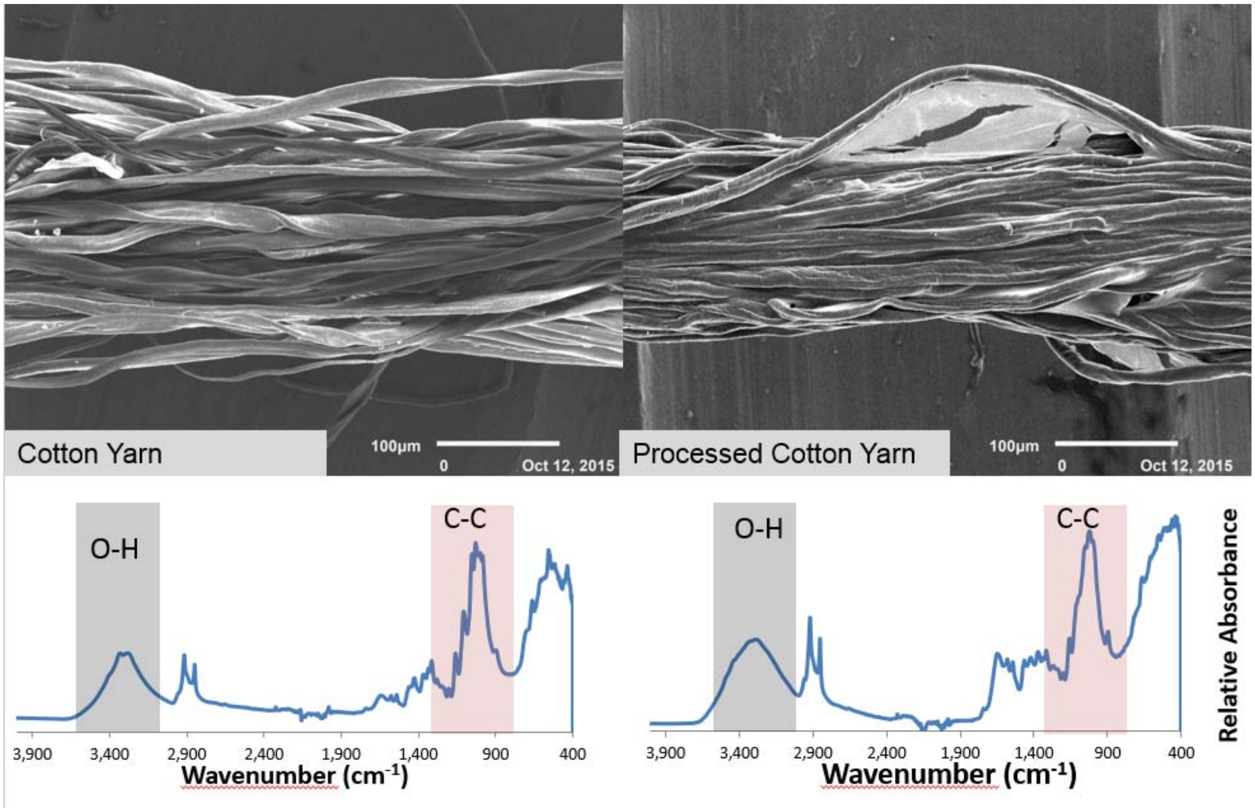

Figure 6: Shown are scanning electron microscopy imaging data as well as IR spectroscopy data for cotton yarn (left, not processed) and cotton yarn processed with an ionic liquid-based solvent (right). The absorbance spectrum for native cotton cloth typical of highly crystalline cellulose I; notably, absorbance due to O-H stretching vibrations at 2600-3500 cm^{-1} as well as C-C stretching and COH and CCH deformation vibrations are observed at 1000-1300 cm^{-1}. The IR spectrum for processed yarn shows hydrogen bonding and crystallinity is decreased in the outer several microns of yarn fibers as cellulose I is converted to cellulose II during processing.

Summary and Ongoing/Future Work

The Thermo Scientific Nicolet iS50R IR Spectrometer has been procured and is greatly enhancing our electrochemistry program at Bradley University. In addition, this spectrometer is providing valuable capabilities to other projects, such as materials science research as well. Going forward, we will continue to utilize work to maximize utilization of this instrument in the following ways:

1) We continue to collect SEIRA data for pure ILs and IL-based systems.

2) We will continue to characterize new biocomposite materials, in particular, materials that have been modified with conductive and catalytic materials so as to operate as composite electrodes.

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